

Processing and Deposition of Nanocrystalline Oxide Composites for  
Thermal Barrier Coatings

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***1. Plasma Spraying of CoNiCrAlY Bond Coat and Electrophoretic Deposition of  
Al<sub>2</sub>O<sub>3</sub>-Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> Nanocomposites***

As described in a previous report [1], electrophoretic deposition (EPD) was used as the method for depositing thermal barrier coatings (TBC). In this report, we used the conventional technique of plasma spraying to deposit a CoNiCrAlY bond coat on the substrates. Following deposition of the plasma sprayed bond coat, electrophoretic deposition was used to deposit Al<sub>2</sub>O<sub>3</sub>-Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> thermal barrier coatings. We examined the thermal stability of the TBC when applied on top of the plasma sprayed CoNiCrAlY-based bond coat. Plasma spraying was compared to electrophoretic deposition as a method for bond coat deposition.

The CoNiCrAlY bond coats were plasma sprayed onto stainless steel substrates by PERMA. The thickness of the plasma sprayed bond coats was ~ 100  $\mu$ m. The bond coats were pretreated at 600 °C in air for 1 hr prior to electrophoretic deposition of the Al<sub>2</sub>O<sub>3</sub>-Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> TBC. For deposition of Al<sub>2</sub>O<sub>3</sub>-Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> nanocomposite, a coating solution consisting of ethanol, water, nitric acid, and the Al<sub>2</sub>O<sub>3</sub>-Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> powder was used. The coating composition was similar to that reported previously [1]. Al<sub>2</sub>O<sub>3</sub>-Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> powder was first mechanically milled for 24 hr to decrease particle size and then added to the coating solution to form a slurry. The slurry was then ultrasonicated for 15 min and aged for 24 hr. Ni electrodes were then lowered into the slurry and a DC voltage (~ 40 V/cm) was applied for 300 sec, resulting in a ~ 50  $\mu$ m-thick coating the Al<sub>2</sub>O<sub>3</sub>-Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> powder. The electrodes were then removed from the slurry, and the coated substrate was dried at 110 °C for 2 hr. Following drying, the coatings were cold isostatically pressed at 50,000 psi to increase mechanical stability.

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## 2. Thermal Stability of Alumina-Yttria-Zirconia Thermal Barrier Coatings

$\text{Al}_2\text{O}_3$ - $\text{Y}_2\text{O}_3$ - $\text{ZrO}_2$  nanocomposite coatings with various  $\text{Al}_2\text{O}_3$  contents were prepared and tested for thermal stability in the presence of the plasma-sprayed bond coat (Table 1). In each case, the  $\text{ZrO}_2$  component contains a low level of  $\text{Y}_2\text{O}_3$  dopants (~1 wt%). Following electrophoretic deposition, the  $\text{Al}_2\text{O}_3$ - $\text{Y}_2\text{O}_3$ - $\text{ZrO}_2$ /CoNiCrAlY-coated Ni substrates were pretreated in argon at 1150 °C for 1 hr (ramp = 10 °C/min). They were then tested for long-term thermal stability by heating to 1150 °C in air (ramp = 10 °C/min). In addition, the coatings were also subjected to thermal cycles of 25 °C-1150 °C-25 °C (with ramping and cooling rates of ~ 300 °C/min) to examine any failure modes due to thermal shock. The samples were inspected visually every hour for spallation of the coating and oxidation of the Ni substrate. All experiments were repeated three times.

The addition of the plasma sprayed bond coat greatly enhanced the thermal stability of the thermal barrier coatings. Coatings prepared with the plasma sprayed bond coats had significantly greater thermal stability, in both coating lifetime and thermal cycling studies, compared with thermal barrier coatings with EPD bond coats (Tables 1 and 2). The thermal barrier coatings with plasma sprayed bond coats were stable up to 14 hr at 1150 °C before visible spallation was observed. The EPD thermal barrier coatings with EPD bond coats lasted up to 6 hr at 1150 °C before failure. Coatings with plasma sprayed bond coats, withstood up to 10 thermal cycles. The EPD coatings tested in this study were fairly similar in stability to those prepared using the conventional plasma spraying. Sun *et al.* tested plasma sprayed coatings containing a CoNiCrAlY-type bond coat and a 8 wt%  $\text{Y}_2\text{O}_3$ -92 wt%  $\text{ZrO}_2$  thermal barrier coating, which lasted for 9 thermal cycles under similar testing conditions before failure (Table 2) [3].

The addition of a small amount of  $\text{Al}_2\text{O}_3$  to the  $\text{ZrO}_2$ -based thermal barrier coatings had a positive effect on the coating lifetime when using bond coats prepared by plasma spraying (Table 1 and 2).  $\text{ZrO}_2$ -based coatings with 5 wt%  $\text{Al}_2\text{O}_3$  began to crack and spall after 12 hr of heat treatment at 1150 °C. The most stable compositions contained 10 wt% and 20 wt%  $\text{Al}_2\text{O}_3$ , which lasted for 14 hr before significant spallation occurred.  $\text{Al}_2\text{O}_3$  addition in TBC also enhanced the thermal shock stability of the plasma sprayed bond coated substrates, as coatings containing 10 wt%  $\text{Al}_2\text{O}_3$  and 20 wt%  $\text{Al}_2\text{O}_3$  withstood 10 thermal cycles before failure. Coatings containing 0 wt% and 5 wt%  $\text{Al}_2\text{O}_3$  spalled after 8 thermal cycles. Thermal stabilization with the addition of  $\text{Al}_2\text{O}_3$  could be explained by a decrease in oxygen conductivity of the nanocomposite thermal barrier coating [2].

Coatings were examined with X-ray diffraction (XRD) to determine the  $\text{ZrO}_2$  phase stability following the heat treatments. Figure 1 shows the XRD patterns of 5 wt%  $\text{Al}_2\text{O}_3$ -1.2 wt%  $\text{Y}_2\text{O}_3$ -93.8 wt%  $\text{ZrO}_2$  coating on plasma sprayed CoNiCrAlY bond coat after 12 hr at 1150 °C. Prior to the heat treatment,  $\text{ZrO}_2$  was present in the tetragonal phase. After 12 hr at 1150 °C,  $\text{ZrO}_2$  still retained 100% tetragonal phase. Other  $\text{Al}_2\text{O}_3$ - $\text{Y}_2\text{O}_3$ - $\text{ZrO}_2$  nanocomposite coatings had the same tetragonal phase present before and after heat treatment at 1150 °C; as no  $\text{ZrO}_2$  phase transformation was noted.

#### ***4. References***

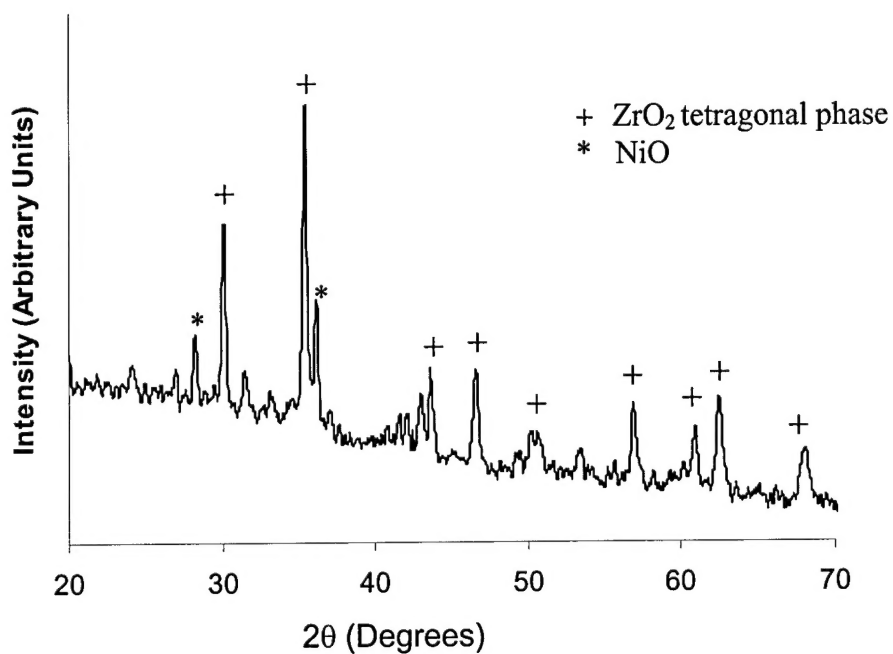
- [1] Ying, J.Y., Technical Report on ONR Grant No. N00014-95-1-0626 for the period of April 1, 2000-June 30, 2000.
- [2] Ying, J.Y., Technical Report on ONR Grant No. N00014-95-1-0626 for the period of January 1, 2000-March 31, 2000.
- [3] Sun, J.H., Chang, E., Chao, C.H., Cheng, M.J., *Oxidation of Metals*, 40 (1993) 465-481.

**Table 1.** Coating lifetime for various alumina-yttria-zirconia nanocomposite thermal barrier coatings deposited by EPD. The bond coat (CoNiCrAlY) was deposited via electrophoretic deposition (EPD) or plasma spraying, as indicated below. The coating lifetime was given by the duration before spallation was first observed for a coating heat treated at 1150 °C in air.

TBC composition	Coating lifetime with bond coat prepared using EPD (hr)	Coating lifetime with bond coat prepared by plasma spraying (hr)
1.3 wt% Y <sub>2</sub> O <sub>3</sub> - 98.7 wt% ZrO <sub>2</sub>	4	12
5 wt% Al <sub>2</sub> O <sub>3</sub> -1.2 wt% Y <sub>2</sub> O <sub>3</sub> -93.8 wt% ZrO <sub>2</sub>	6	12
10 wt% Al <sub>2</sub> O <sub>3</sub> -1.2 wt% Y <sub>2</sub> O <sub>3</sub> -88.8 wt% ZrO <sub>2</sub>	6	14
20 wt% Al <sub>2</sub> O <sub>3</sub> -1.0 wt% Y <sub>2</sub> O <sub>3</sub> -79.0 wt% ZrO <sub>2</sub>	2	14
100 wt% Al <sub>2</sub> O <sub>3</sub>	1	--

**Table 2.** Thermal shock stability for various alumina-yttria-zirconia nanocomposite thermal barrier coatings deposited by EPD. The number of cycles to failure was given by the number of thermal cycles prior to the observation of spallation. A thermal cycle involved heating the sample in air from 25 °C to 1150 °C, holding at 1150 °C for one hour, and then cooling to 25 °C, with ramping and cooling rates of ~ 300 °C/min. The Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> coating tested by Sun *et al.* [3] was prepared using plasma spraying, as opposed to EPD.

TBC composition	Cycles to failure with bond coat prepared using EPD (hr)	Cycles to failure with bond coat prepared by plasma spraying (hr)
1.3 wt% Y <sub>2</sub> O <sub>3</sub> - 98.7 wt% ZrO <sub>2</sub>	1	8
5 wt% Al <sub>2</sub> O <sub>3</sub> -1.2 wt% Y <sub>2</sub> O <sub>3</sub> -93.8 wt% ZrO <sub>2</sub>	3	8
10 wt% Al <sub>2</sub> O <sub>3</sub> -1.2 wt% Y <sub>2</sub> O <sub>3</sub> -88.8 wt% ZrO <sub>2</sub>	3	10
20 wt% Al <sub>2</sub> O <sub>3</sub> -1.0 wt% Y <sub>2</sub> O <sub>3</sub> -79.0 wt% ZrO <sub>2</sub>	1	10
100 wt% Al <sub>2</sub> O <sub>3</sub>	<1	--
8 wt% Y <sub>2</sub> O <sub>3</sub> -92 wt% ZrO <sub>2</sub> (Sun <i>et al.</i> [3])	--	9



**Figure 1.** X-ray diffraction patterns of 5 wt% Al<sub>2</sub>O<sub>3</sub>-1.2 wt% Y<sub>2</sub>O<sub>3</sub>-93.8 wt% ZrO<sub>2</sub> TBC electrophoretically deposited on Ni substrate with the plasma sprayed CoNiCrAlY bond coat following 12 hours of heat treatment at 1150 °C.